Relative low-temperature synthesis of lead titanate ($PbTiO_3$) whiskers via flux method

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Well dispersive and single-crystal lead titanate ($PbTiO_3$) whiskers were successfully synthesised by sintering lead acetate and titanium dioxide with improvement of adding potassium chloride as flux at a relatively low temperature. The starting materials were homogenised by different molar ratios and the as-prepared samples were pre-treated before characterising by X-ray diffraction, a scanning electron microscope and a transmission electron microscope. Comparison experiments indicated that the temperature and the amount of flux played an important role in determining the morphology and purity of the products. A liquid–solid growth mechanism is proposed for formation of $PbTiO_3$ whiskers.

1. Introduction: One-dimensional (1D) inorganic materials such as nanowires and whiskers have attracted widespread attention owing to their specific physical, chemical, mechanical, optical and electrical performances [1, 2]. Perovskite-type material with the chemical formula of ABO_3 is one of the most significant functional materials in the solid-state chemistry field.

It has been proved that perovskite structure lead titanate ($PbTiO_3$ or PT)-based ceramics could exhibit outstanding dielectric, piezoelectric, pyroelectric and photoelectric properties for applications in electronics and electro-optic devices at high temperatures and frequencies. Dense perovskite lead titanate (PT), together with $BaTiO_3$, $SrTiO_3$, $CaTiO_3$ and $CaCu_3Ti_4O_{12}$, is widely used in electronic and microelectronic ceramics [3–11]. However, problems coexist with the thermal expansion mismatch and mechanical stretching force. To strengthen the properties of the matrix composites, several attempts have been utilised by addition of the matching polymers, metals, fibres or whiskers.

Traditionally, $PbTiO_3$ was prepared by hydrothermal (solvothermal) and sol–gel methods to obtain the precursors and then calcined at certain temperature ranges [12–16]. However, almost all these wet-chemistry routes required the precursors to be calcined in the temperature range of 600–1500°C, although these products have controlled morphology and stoichiometry, yet this procedure was not easy to obtain the heat resisting materials and the large particles may limit their applications in electronic devices. The fibre-like PT whiskers, with relative good toughness and mechanical intensity have potential applications in ceramic-based functional composites to remedy and enhance the defects of the body-materials.

In our experiment, titanium dioxide (TiO_2), lead acetate ($Pb(CH_3COO)_2{\cdot}3H_2O$) together with potassium chloride (KCl) were chosen as the starting materials. By adjusting the molar ratios of the materials and the sintering temperatures, well-crystallised PT whiskers were synthesised.

2. Experimental work: [$Pb(CH_3COO)_2{\cdot}3H_2O$], ($TiO_2$) and KCl were all analytical grade reagents without further purification. The raw materials were actually weighed by adjusting the raw molar ratio of Pb:Ti:KCl = 1:1:5–10. A mortar was used to grind the raw materials to make them well-mixed. The pre-treated reactants with different molar ratios were transferred into the corundum crucible, no other additives were added. The mixtures were sintered, respectively, at different temperature ranges (the same heating rate of 5°C/min) in the muffle furnace for 5 h, and then cooled down to room temperature. The dark yellow products were obtained, which were immersed and washed several times by hot deionised water to get rid of the flux until no free chloride ions were detected by silver nitrate titration. Then, the filtrated samples were dried at 100°C for 2 h before further identification.

The phase of the as-prepared products were identified by X-ray diffraction (XRD) (D/MAX 2500, Japan) with Cu$K\alpha$ radiation at a scanning speed of 8°/min. The morphology was characterised by the scanning electron microscope (SEM, JSM-5610LV, Japan). The microstructure was detected by a field emission transmission electron microscope (FETEM, Tecnai G2 F20 S-TWIN, America).

3. Results and discussion

3.1. Microstructure characterisation: Fig. 1 shows the XRD patterns of the as-prepared samples sintered at different temperatures. The main diffraction peaks of the products obtained under different sintering conditions matched well with the standard $PbTiO_3$ spectra (space group $P_{4\,mm}$, JCPDS No. 10-73-7550), which indicated that the reaction temperature range and the Ti/Pb of 1:1 were agreeable for the formation of $PbTiO_3$. The XRD patterns of the whiskers (Pb:Ti:KCl = 1:1:10, 850°C for 5 h) indicated that the diffraction intensities of the (100), (110), (111), (200), (210), (301) and (222) planes were the dominant peaks (shown in Fig. 2); the as-prepared $PbTiO_3$ has a cubic perovskite structure.

The influences of temperature and the molar ratios are shown in Fig. 3. The morphology and purity would be significantly improved with the increase of temperature and the quality of flux. Figs. 3*a* and *b* indicate that when Pb:Ti:KCl = 1:1:5, the synthesis temperature ranges of 780–800°C, most of the products interlaced together to

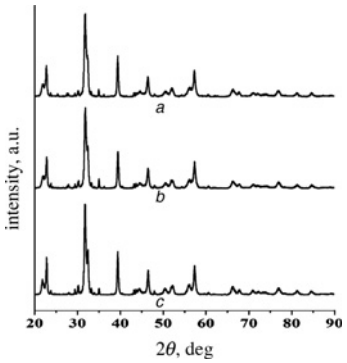

Figure 1 *XRD patterns of the products obtained at different temperatures*
a 780°C, Ti:Pb:KCl = 1:1:5
b 830°C, Ti:Pb:KCl = 1:1:8
c 850°C, Ti:Pb:KCl = 1:1:10

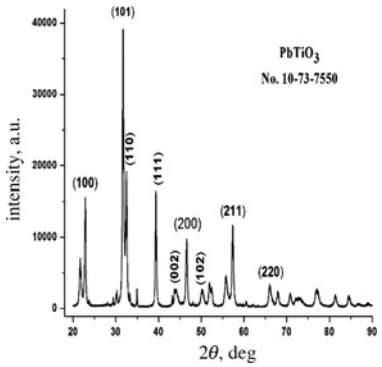

Figure 2 *XRD patterns of the PT whiskers with diffraction intensities*

form large particles and less whiskers with lengths of 10–50 μm. As shown in Figs. 3*c* and *d*, PT whisker formation was improved with the flux increasing at 830°C, the average length of the single whisker was 5 μm, yet the purity and surface smoothness were not enhanced. As shown in Figs. 3*e* and *f*, the well-crystallised single PT whisker with a length of 10–20 μm formed at 850°C.

Temperature was one of the sensitive factors in synthesising crystal materials via the flux method. In our experiment, KCl was chosen as the flux, whose melting point was 785°C. With the increase of temperature, KCl formed molten salt for dissolution of TiO_2 and $Pb(Ac)_2$, at the same time, $Pb(Ac)_2$ decomposed in the form of PbO, CO and CO_2, which promoted the chemical reaction. When the temperature reached 850°C, the raw materials were all thermally activated and the molten salt environment accelerated the dissolution-crystallisation rate. TiO_2 and PbO reacted to form $PbTiO_3$ particles. With the energy supply of the calcination temperature, large scale of the particles took the shape of the needle-like crystals and grew along the 1D direction. The purity of $PbTiO_3$ whiskers was improved by the temperature.

The influence of the molar ratios of the raw materials on the morphology of the products could be explained as follows. In the whole experiment, the molar ratio of Ti:Pb was controlled by 1:1, the molar of the flux affected the generation of PT whiskers. The flux melted at its melting point to form the liquid phase for dissolution of the raw materials. The nucleation and growth process took place in the molten salt system, and the sufficient amount of flux was promising for the growth of PT whiskers.

Comparison experiments were employed to verify the influence of the sintering temperature. We controlled Ti:Pb:KCl = 1:1:10, sintering at 900 and 950°C, respectively, for 5 h (a heating rate of 5°C/min). With the temperature increasing, the flux violated gradually, which disturbed the growth environment of PT whiskers, thus forming flaky crystals and the needle-like PT whiskers decreased significantly as shown in Figs. 4*a* and *b*, which was not favourable for 1D growth.

The TEM images of the pure phase $PbTiO_3$ sintered at 850°C for 5 h with the molar ratio of Ti:Pb:KCl = 1:1:10 are shown in Fig. 5. The diameter of the PT whiskers ranged from 50 to 100 nm. The layers of the whiskers produced a well-crystallised structure. The legible lattice fringes with an interplannar spacing of 0.407 nm are quite similar to the standard value of the (100) planes of the perovskite $PbTiO_3$ (0.4058 nm).

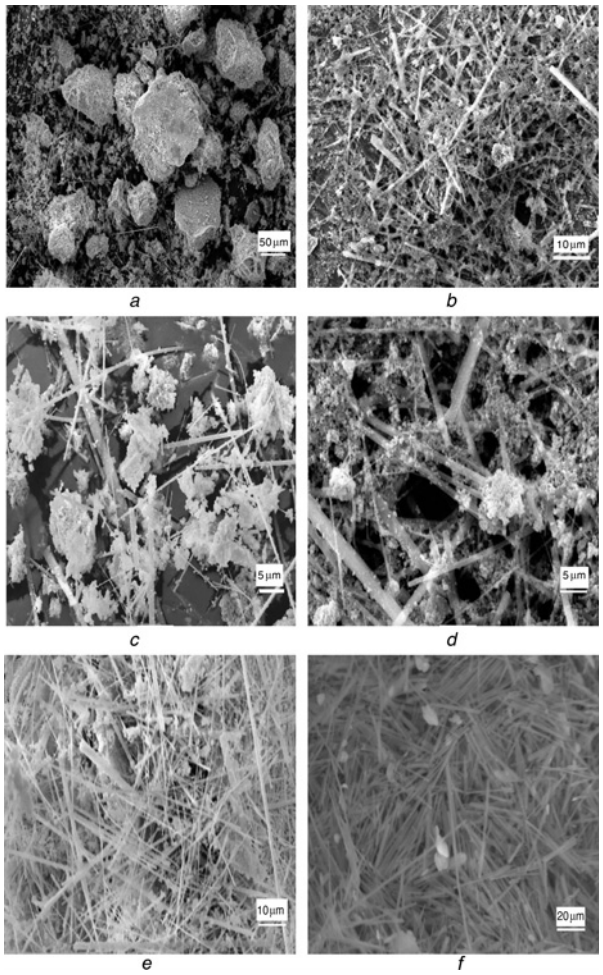

Figure 3 *SEM images of the products calcined under different molar ratios and temperatures*
a 780°C, Ti:Pb:KCl = 1:1:5
b 800°C, Ti:Pb:KCl = 1:1:5
c 830°C, Ti:Pb:KCl = 1:1:8
d 830°C, Ti:Pb:KCl = 1:1:10
e 850°C, Ti:Pb:KCl = 1:1:8
f 850°C, Ti:Pb:KCl = 1:1:10

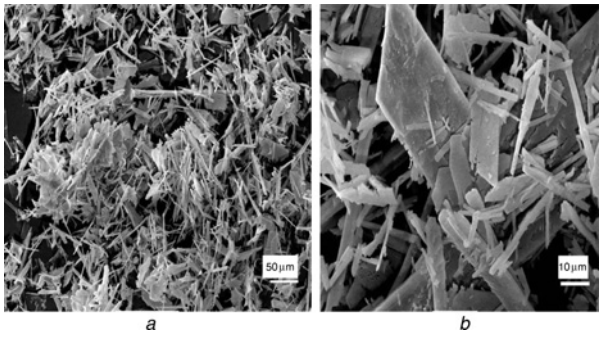

Figure 4 *SEM images of products obtained at different sintering conditions*
a Ti:Pb:KCl = 1:1:10, 900°C
b Ti:Pb:KCl = 1:1:10, 950°C

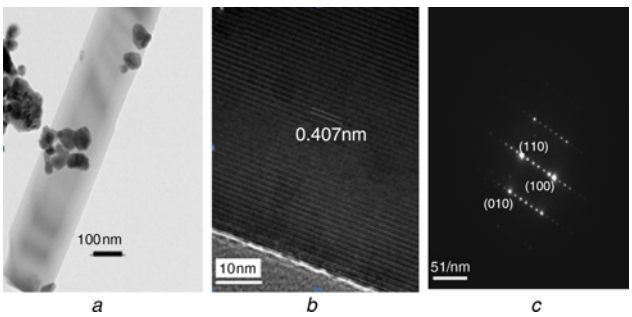

Figure 5 *Bright-field TEM micrograph (Fig. 5a); lattice image of a typical $PbTiO_3$ whisker (Fig. 5b); selected area electron diffraction pattern (Fig. 5c)*

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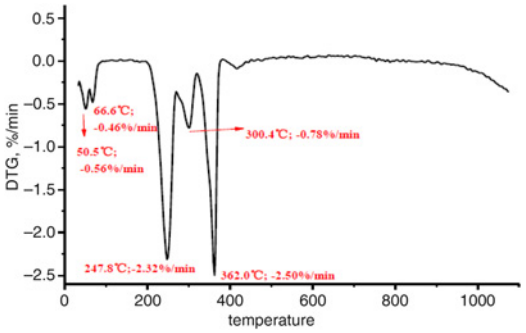

Figure 6 *DSC curve of $Pb(CH_3COO)_2{\cdot}3H_2O$*

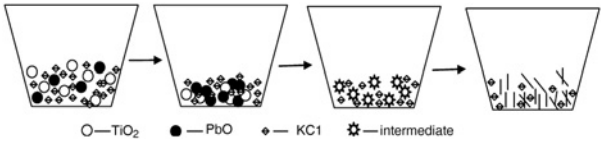

Figure 7 *Schematic diagram for the growth of $PbTiO_3$ whiskers in the corundum crucible*

3.2. Analysis of whisker growth: A DSC curve of the Pb $(CH_3COO)_2{\cdot}3H_2O$ was given to assist in the interpretation of the growth mechanism (Fig. 6). $Pb(Ac)_2{\cdot}3H_2O$ dehydrated at 50–247°C, the three molar crystal water was gradually released. Then Pb $(CH_3COO)_2$ decomposed in the form of PbO, CO and CO_2 at 300–360°C, the gas phase volatilised, only leaving the activated PbO.

The formation of PT whiskers could be explained by the following reaction equations

$$Pb(CH_3COO)_2{\cdot}3H_2O(s) \rightarrow PbC_2O_4(s) + 3H_2O(g) \quad (1)$$

$$PbC_2O_4(s) \rightarrow PbO(s) + CO(g) + CO_2(g) \quad (2)$$

$$PbO(s) + TiO_2(s) \rightarrow PbTiO_3(s) \quad (3)$$

In our reaction system, the flux provided a liquid phase medium for the reactants' dissolution, diffusion and precipitation above its melting point. A liquid–solid (LS) reaction mechanism was appropriate for the formation of $PbTiO_3$ whiskers.

The schematic diagram shown in Fig. 7 clearly demonstrates the formation of PT whiskers. When the temperature reached 780°C, the flux KCl melted to form a liquid phase. As the temperature increased, the activated TiO_2 and PbO began to collide with each other from different directions and combined to form the needle-like $PbTiO_3$ with the energy supply of the holding temperature. The molten salt offered super saturation to promote whisker formation. Comparison tests confirmed that the molten salt gradually volatilised with the temperature rising, which destroyed the growth environment for PT whiskers and affected the morphology of the products.

4. Conclusions: The single-crystal $PbTiO_3$ whiskers with a length of 10–20 μm were synthesised via the flux method. The synthesis process was straightforward and the sintering condition was moderate. Comparison experiments proved that the optimum reaction condition was Ti:Pb:KCl = 1:1:10, a holding temperature of 850°C for 5 h. The temperature and the amount of the flux were the key factors to determine the morphology and purity of the PT whiskers. The growth process was concluded as a LS mechanism with the assistance of molten salt. This flux route has potential prospects for application.

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